

(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 178 030 A2

9

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
06.02.2002 Bulletin 2002/06(51) Int Cl.7: C07C 41/01, C07C 41/40,  
C07C 41/42, C07C 43/13

(21) Application number: 01118203.7

(22) Date of filing: 28.07.2001

(84) Designated Contracting States:  
 AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
 MC NL PT SE TR  
 Designated Extension States:  
 AL LT LV MK RO SI

(30) Priority: 03.08.2000 JP 2000235578  
 03.08.2000 JP 2000235580  
 03.08.2000 JP 2000235582  
 03.08.2000 JP 2000235583  
 03.08.2000 JP 2000235584

(71) Applicant: MITSUBISHI GAS CHEMICAL  
 COMPANY, INC.  
 Chiyoda-ku, Tokyo (JP)

(72) Inventors:  
 • Ninomiya, Teruyuki  
 Kurashiki-shi, Okayama (JP)  
 • Watanabe, Toshio  
 Kurashiki-shi, Okayama (JP)  
 • Iwamoto, Atsushi  
 Kurashiki-shi, Okayama (JP)  
 • Miyashita, Soemu  
 Kurashiki-shi, Okayama (JP)  
 • Watanabe, Masafumi  
 Kurashiki-shi, Okayama (JP)

(74) Representative:  
 Gille Hrabal Struck Neidlein Prop Roos  
 Patentanwälte Brucknerstrasse 20  
 40593 Düsseldorf (DE)

## (54) Process for recovering ditrimethylolpropane

(57) The present invention provides processes for recovering ditrimethylolpropane from a still residue obtained by extracting and then distilling off trimethylolpropane from a reaction solution obtained by reacting n-butyaldehyde with formaldehyde in the presence of a basic catalyst.

One process comprises acid decomposition of formals

in the still residue.

A second process comprises removal from the still residue of components having a higher boiling point than that of ditrimethylolpropane followed by crystallization of the resultant product.

BEST AVAILABLE COPY

compound contained in the still residue to acid decomposition; ii) removing high-boiling components having a higher boiling point than that of ditrimethylolpropane, from the still residue, and iii) subjecting the resultant product to crystallization using a solvent;

(5) a process according to any one of the above aspects (1) to (3), wherein after the formal compound contained in a distillate obtained by removing the high-boiling components having a higher boiling point than that of ditrimethylolpropane, is subjected to acid decomposition, the resultant product is subjected to crystallization using a solvent;

(6) a process according to the above aspect (4) or (5), wherein the removal of the high-boiling components having a higher boiling point than that of ditrimethylolpropane, is performed by molecular distillation;

(7) a process according to any one of the above aspects (1) to (3), wherein after the still residue is first subjected to crystallization using a solvent and then the formal compound contained in the resultant crystallized product is subjected to acid decomposition, the resultant reaction mixture obtained from the acid decomposition is subjected to crystallization;

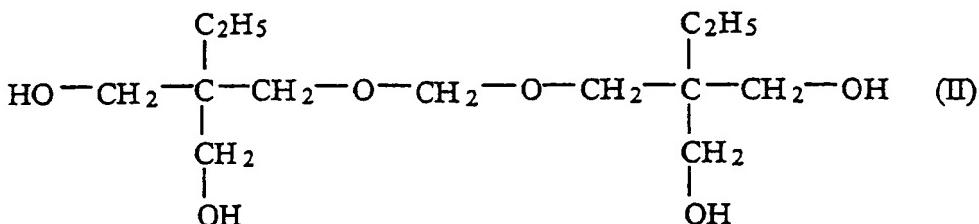
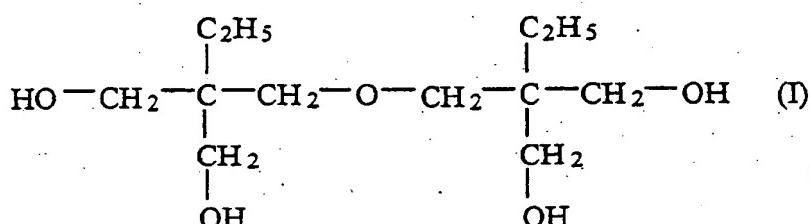
(8) a process for recovering ditrimethylolpropane from a still residue obtained by extracting and then distilling off trimethylolpropane from a reaction solution obtained by reacting n-butyraldehyde with formaldehyde in the presence of a basic catalyst, said process comprising: removing high-boiling components having a higher boiling point than that of ditrimethylolpropane, from the still residue, and subjecting the resultant product to crystallization;

(9) a process according to the above aspect (8), wherein the removal of the high-boiling components having a higher boiling point than that of ditrimethylolpropane, is performed by molecular distillation ; and

(10) a process according to the above aspect (8) or (9), wherein the solvent used upon the crystallization is water.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0009] The ditrimethylolpropane (di-TMP) of the present invention and bistrimethylolpropane (bis-TMP), are represented by the following formulae (I) and (II), respectively.



[0010] In the process of the present invention, when TMP is separated from a reaction solution obtained by the reaction between NBD and formaldehyde, the reaction solution in either concentrated or non-concentrated state is subjected to extraction with a solvent to obtain a TMP extract (crude TMP) containing substantially no sodium formate.

[0011] Examples of the solvent used upon the extraction of TMP include aliphatic esters such as butyl acetate and ethyl acetate; aliphatic ketones such as methylethyl ketone, methylisobutyl ketone and diisopropyl ketone; alcohols such as isobutanol, amyl alcohol, hexyl alcohol and cyclohexanol; aldehydes such as isobutyraldehyde and n-butyraldehyde; and mixed solvents thereof.

[0012] The crude TMP produced by extracting TMP from the reaction solution obtained by the reaction between NBD and formaldehyde, is purified by distillation under high vacuum to separate a TMP product from the still residue. The di-TMP is recovered from the still residue.

**BEST AVAILABLE COPY**

- [0023] After completion of the acid decomposition reaction, the resultant reaction mixture was successively subjected to neutralization, removal of low-boiling components and removal of salts and high-boiling components having a higher boiling point than that of di-TMP to obtain a high-purity di-TMP.
- [0024] As the neutralizer, there may be used aqueous solutions of sodium carbonate, sodium hydrogencarbonate, sodium hydroxide or the like.
- [0025] The neutralization procedure may be conducted by adding the neutralizer little by little to the reaction mixture obtained by the acid decomposition reaction, and continued until the pH value thereof reaches 7.
- [0026] The low-boiling components may be removed by distillation. Here, the "low-boiling components" mean those components having a lower boiling point than that of di-TMP, and mainly include CMF and TMP. These low-boiling components may be readily removed by distillation since the boiling points thereof are far lower than that of di-TMP. The distillation temperature is in the range of 140 to 200°C, preferably 150 to 180°C, and the distillation pressure is 670 Pa or lower, preferably 130 Pa or lower.
- [0027] The removal of the salts and the high-boiling components having a higher boiling point than that of di-TMP may be effectively conducted by molecular distillation, specially film evaporator. The temperature used for the film evaporator is in the range of 130 to 280°C, preferably 160 to 250°C, and the pressure is 130 Pa or lower.
- [0028] Also, in the first invention, the reaction mixture obtained by the acid decomposition reaction may be subjected to crystallization by adding a solvent thereto to obtain purified di-TMP.
- [0029] Examples of the solvent used for the crystallization of di-TMP include organic solvents, e.g., aliphatic ethers such as dioxane and tetrahydrofuran; aliphatic esters such as ethyl acetate and butyl acetate; aliphatic ketones such as acetone and methylisobutyl ketone; and aliphatic alcohols such as hexyl alcohol and heptyl alcohol. These solvents may be used alone or in the form of a mixture of any two or more thereof.
- [0030] The amount of the solvent used is 0.5 to 10 parts by weight, preferably 1 to 4 parts by weight based on one part by weight of the still residue obtained after the recovery of TMP. When the amount of the solvent used is less than 0.5 part by weight, the resultant crystals are deteriorated in quality, or no crystals are obtainable. When the amount of the solvent used is more than 10 parts by weight, the burden required for the recovery of the solvent becomes large, resulting in industrially disadvantageous process.
- [0031] In the crystallization of di-TMP, the reaction mixture obtained by the acid decomposition reaction is mixed with the solvent under heating until a transparent solution is obtained. Then, the resultant solution is slowly cooled while stirring. In this case, the reaction mixture is usually heated to a temperature of 60 to 80°C, and then the resultant solution is cooled to about room temperature. In order to obtain the crystals at higher yield, the solution is cooled to a temperature lower than room temperature, preferably 0 to 1°C. The thus obtained crystals are washed, filtered, centrifugally separated and then dried to obtain a high-purity di-TMP.
- [0032] Meanwhile, the crystal-washing solution obtained upon the crystallization of di-TMP and the solvent recovered upon the drying may be reused as the solvent for the crystallization.
- [0033] In the first invention, when the acid and/or the hydroxylamine salt is added to the still residue obtained after distilling off TMP; bis-TMP may be selectively decomposed. Therefore, it becomes possible to readily obtain a high-purity di-TMP.
- [0034] Further, in the first invention, the formation of CDF is avoided by adding the scavenger for decomposed products during the acid decomposition reaction, so that the di-TMP is produced at a high yield. Accordingly, in the first invention, even if the still residue obtained after distilling off TMP contains a considerable amount of bis-TMP, it is possible to obtain a high-quality di-TMP therefrom at a high yield.
- [0035] Furthermore, since the process according to the first invention comprises the steps of i) subjecting the formal compound contained in the still residue to acid decomposition; ii) removing high-boiling components having a higher boiling point than that of ditrimethylolpropane, from the still residue; and iii) subjecting the resultant product to crystallization using a solvent, it is possible to effectively recover the di-TMP.
- [0036] The present inventors have found that coloring components contained in the di-TMP products are compounds having a higher boiling point than that of di-TMP. Therefore, it is desirable to previously remove the high-boiling components from the still residue before the acid decomposition reaction. The removal of the high-boiling components from the still residue before the acid decomposition reaction may be suitably performed by either distillation or crystallization using a solvent. When the high-boiling components are removed from the still residue, substantially whole amounts of coloring components and salts such as sodium formate can be eliminated therefrom.
- [0037] In the case where the high-boiling components are removed from the still residue by distillation, molecular distillation, specially the film evaporator is used to effectively distill off di-TMP. The temperature used for the film evaporator is in the range of 130 to 280°C, preferably 160 to 250°C, and the pressure used therefor is 130 Pa or lower. As the temperature for the film evaporator is lowered, the ratio of bis-TMP to di-TMP on the distillate side is reduced, so that the removal efficiency of the coloring components is improved.
- [0038] When the high-boiling components are removed from the still residue by crystallization using a solvent, the crystallization may be performed in the substantially same manner as the above crystallization procedure conducted

BEST AVAILABLE COPY

## PRODUCTION EXAMPLE

[0051] TMP was produced by reacting n-butyraldehyde with formaldehyde by the method described in Japanese Patent Application Laid-open No. Heisei 11 (1999)-49708. After completion of the reaction, the raw materials as low-boiling components were recovered and by-products were removed from the reaction solution, and then the resultant crude TMP was distilled by a film evaporator. The obtained still residue had the following composition:

TMP	10.0%
di-TMP	39.6%
bis-TMP	30.8%
Other organic by-products	19.6%
Salts	3,000 ppm
Coloring degree (Gardner color scale)	18

## EXAMPLE 1

[0052] A 50-ml Erlenmeyer flask was charged with 10.0 g of the still residue obtained in PRODUCTION EXAMPLE, 3.0 g of hydroxylamine sulfate and 17.0 g of water, and the contents of the flask were heated at 90°C for 3 hours under stirring to conduct an acid decomposition reaction thereof. After completion of the reaction, the reaction mixture was measured by gas chromatography (hereinafter referred to merely as "GC") to examine its composition. As a result, it was confirmed that no di-TMP was decomposed, but bis-TMP and other components similar to di-TMP were completely decomposed and converted into low-boiling components such as TMP. In addition, it was confirmed that no CDF was produced by the acid decomposition reaction. After neutralizing the reaction mixture with a saturated sodium hydrogencarbonate aqueous solution, low-boiling and high-boiling components were removed therefrom, so that di-TMP having a purity of 98.3% and a Hazen color scale of 50 or lower was obtained at a recovery percentage of 80%.

## EXAMPLE 2

[0053] A 1.000-ml three-neck flask equipped with a reflux condenser and a magnetic stirrer, was charged with 201.3 g of the still residue obtained in PRODUCTION EXAMPLE, 404.9 g of methanol and 4.0 g of sulfuric acid. The contents of the flask were heated under stirring at such a temperature capable of causing methanol to be refluxed, thereby subjecting them to acid decomposition reaction for 2 hours. Dimethoxymethane produced during the reaction was continuously discharged out of the reaction system. After completion of the reaction, the obtained reaction mixture was measured by gas chromatography (GC) to examine its composition. As a result, it was confirmed that bis-TMP and other components similar to di-TMP were completely decomposed, and that the ratio of di-TMP to CDF was 4.3:1. After the reaction mixture was neutralized with a saturated sodium hydrogencarbonate aqueous solution, low-boiling and high-boiling components were removed therefrom. As a result, di-TMP having a purity of 98.5% and a Hazen color scale of 50 or lower was obtained at a recovery percentage of 60%.

## COMPARATIVE EXAMPLE 1

[0054] A 500-ml beaker equipped with a mechanical stirrer was charged with 150 g of the still residue obtained in PRODUCTION EXAMPLE and 150 g of methylisobutyl ketone (MIBK), and the contents of the flask were heated under stirring until a transparent solution was obtained. Then, the resultant solution was slowly cooled to 20°C for about 3 hours under stirring. The obtained crystals were washed with 75 g of MIBK and then dried under reduced pressure to recover about 90% of di-TMP and bis-TMP contained in the still residue. Sixty six grams of the obtained crystals were dissolved in 132 g of water at 50°C, and the resultant solution was slowly cooled to 20°C under stirring. The obtained crystals were washed with 66 g of water and then dried. As a result, it was confirmed that 30.9 g of crystals having a purity of 90.1% or higher when measured by GC and a Hazen color scale of about 130 were obtained, and the recovery percentage of di-TMP was 40%.

[0055] Meanwhile, EXAMPLE 1 shows the case where the acid decomposition was conducted by adding a scavenger for decomposed products to the still residue produced upon the purification of TMP; EXAMPLE 2 shows the case where the acid decomposition was conducted without using the scavenger for decomposed products; and COMPARATIVE EXAMPLE 1 shows the case where no acid decomposition was conducted. From the above results, it was confirmed that when the scavenger for decomposed products was added to the still residue upon the acid decomposition thereof in accordance with the present invention, it became possible to effectively remove impurities therefrom and obtain a high-purity di-TMP at a high yield.

BEST AVAILABLE COPY

5

TMP	32.6%
di-TMP	46.1%
CMF	10.7%
bis-TMP	0.0%
Other organic by-products	10.6%

[0062] The reaction mixture obtained after the acid decomposition was mixed with 60.0 g of ethyl acetate, and then heated to a temperature of 50 to 60°C while stirring to obtain a uniform solution. The solution was then gradually cooled to 20°C while stirring for 4 hours to obtain crystals. The obtained crystals were filtered out, washed with ethyl acetate, and then dried under reduced pressure to obtain 15.2 g of white di-TMP powder having a purity of 98.5%. Also, it was confirmed that the obtained di-TMP was a high-purity product exhibiting a melting point of 109.2 to 110.2°C and exhibited a Hazen color scale 20 or lower. The recovery percentage of di-TMP was 42%

15

## EXAMPLE 6

[0063] A 500-ml beaker equipped with a magnetic stirrer was charged with 180 g of the still residue obtained in PRODUCTION EXAMPLE and 180 g of methylisobutyl ketone (MIBK), and the contents of the beaker were heated to a temperature of 50 to 60°C while stirring to completely dissolve the still residue in MIBK. The resultant solution was gradually cooled to 20°C for 4 hours while stirring to obtain crystals. The obtained crystals were filtered out, washed with MIBK and then dried to obtain 94 g of crystals. After heating the crystals to 100°C, 330 mg (3,500 ppm) of p-toluenesulfonic acid was added thereto, and the mixture was subjected to acid decomposition reaction at 90°C for 2 hours.

25

[0064] The reaction solution obtained after the acid decomposition reaction was distilled at 140°C under a pressure of 13 Pa to recover low-boiling components (mainly CMF) therefrom. Then, the solution was cooled to about 100°C, and 110 g of MIBK was added thereto. The resultant mixture was stirred under heating at about 100°C to obtain a uniform solution. The obtained solution was cooled to 20°C for 3 hours while stirring to obtain crystals. The crystals were filtered out, washed with MIBK, and then dried under reduced pressure to obtain 45.2 g of white di-TMP powder having a purity of 98.4% and a Hazen color scale of 30 or lower. The recovery percentage of di-TMP was 63%

30

## EXAMPLE 7

35

[0065] The still residue obtained in PRODUCTION EXAMPLE was subjected to film evaporator at 235°C under a pressure of 13 Pa or lower to remove high-boiling components having a higher boiling point than that of di-TMP together with salts therefrom. The obtained distillate was further distilled at 180°C under a pressure of 13 Pa or lower to recover TMP therefrom. Forty nine grams of water was added to 49.0 g of the resultant bottoms, and the mixture was heated while stirring until a transparent solution was obtained. The obtained solution was slowly cooled to 0°C for 6 hours while stirring. The resultant crystals were filtered out, washed with water, and then dried to obtain 5.9 g of crystals. It was confirmed that the crystals were di-TMP having a purity of 95.4%, and exhibited a Hazen color scale of 50 or lower. The recovery percentage of di-TMP was 26%

40

## COMPARATIVE EXAMPLE 3

45

[0066] One thousand grams of the still residue obtained in PRODUCTION EXAMPLE was dissolved in 1,000 g of ethyl acetate under heating. The obtained solution was slowly cooled to 20°C while stirring, and further continuously stirred at 20°C for a while. After 6 hours, the obtained crystals were filtered out, sufficiently washed with 1,000 g of ethyl acetate, and then dried to obtain 52 g of crystals. It was confirmed that the resultant crystals contained 57.1% of di-TMP and 39.3% of bis-TMP, and exhibited a Hazen color scale of about 150. The recovery percentage of di-TMP was 75%.

50

[0067] EXAMPLE 4 shows the case where the still residue obtained upon the purification of TMP was successively subjected to film evaporator in order to remove high-boiling components therefrom, to acid decomposition in order to decompose a formal compound contained therein, and then to crystallization; EXAMPLES 5 and 6 shows the case where the still residue obtained upon the purification of TMP was successively subjected to crystallization using a solvent, to acid decomposition and then again to crystallization; and EXAMPLE 7 show the case where the still residue obtained upon the purification of TMP was subjected to film evaporator in order to remove high-boiling components therefrom, and then to crystallization. From the above results, it was confirmed that di-TMP obtained in each of these EXAMPLES exhibited a lower coloring degree and had a higher purity as compared to that obtained in COMPARATIVE

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)



EP 1 178 030 A3

(12)

## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
27.03.2002 Bulletin 2002/13

(51) Int Cl.<sup>7</sup>: C07C 41/01, C07C 41/40,  
C07C 41/42, C07C 43/13

(43) Date of publication A2:  
06.02.2002 Bulletin 2002/06

(21) Application number: 01118203.7

(22) Date of filing: 28.07.2001

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 03.08.2000 JP 2000235578  
03.08.2000 JP 2000235580  
03.08.2000 JP 2000235582  
03.08.2000 JP 2000235583  
03.08.2000 JP 2000235584

(71) Applicant: MITSUBISHI GAS CHEMICAL  
COMPANY, INC.  
Chiyoda-ku, Tokyo (JP)

(72) Inventors:  
• Ninomiya, Teruyuki  
Kurashiki-shi, Okayama (JP)  
• Watanabe, Toshio  
Kurashiki-shi, Okayama (JP)  
• Iwamoto, Atsushi  
Kurashiki-shi, Okayama (JP)  
• Miyashita, Soemu  
Kurashiki-shi, Okayama (JP)  
• Watanabe, Masafumi  
Kurashiki-shi, Okayama (JP)

(74) Representative:  
Gille Hrabal Struck Neidlein Prop Roos  
Patentanwälte  
Brucknerstrasse 20  
40593 Düsseldorf (DE)

### (54) Process for recovering ditrimethylolpropane

(57) The present invention provides processes for recovering ditrimethylolpropane from a still residue obtained by extracting and then distilling off trimethylolpropane from a reaction solution obtained by reacting n-butyraldehyde with formaldehyde in the presence of a basic catalyst.

One process comprises acid decomposition of formals

in the still residue.

A second process comprises removal from the still residue of components having a higher boiling point than that of ditrimethylolpropane followed by crystallization of the resultant product.

EP 1 178 030 A3

BEST AVAILABLE COPY



European Patent  
Office

Application Number

EP 01 11 8203

### CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
  
- No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

### LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
  
- As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
  
- Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
  
- None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

**BEST AVAILABLE COPY**

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 01 11 8203

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-01-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
GB 1292405	A	11-10-1972	JP DE NL SE	49024043 B 2058519 A1 7017369 A 370934 B	20-06-1974 09-06-1971 02-06-1971 04-11-1974
GB 1291335	A	04-10-1972	JP DE NL SE US	49024044 B 2058518 A1 7017225 A 370540 B 3740322 A	20-06-1974 09-06-1971 02-06-1971 21-10-1974 19-06-1973
US 3829507	A	13-08-1974	DE	2212793 A1	28-09-1972
US 3962347	A	08-06-1976	SE DE IT JP JP JP	370388 B 2358297 A1 1001789 B 1142823 C 49133311 A 57036259 B	14-10-1974 30-05-1974 30-04-1976 13-04-1983 21-12-1974 03-08-1982